

²⁷Al, ^{47,49}Ti, ³¹P, AND ¹³C MAS NMR STUDY OF VX, GB, GD AND HD REACTIONS WITH
NANOSIZE Al₂O₃, Al₂O₃, TiO₂, ALUMINUM AND TITANIUM

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ABSTRACT

Assorted reactions of VX, GB, GD and HD with Al₂O₃, TiO₂ (anatase and rutile), aluminum and titanium metal powders have been studied by ²⁷Al, ^{47,49}Ti, ³¹P and ¹³C MAS NMR. VX, GB, GD and HD hydrolyze on both nanosize and conventional Al₂O₃. A significant droplet size effect on the reaction kinetics is observed. For VX, GB and GD, ²⁷Al and ³¹P MAS NMR detect the formation of stable, precipitated aluminum phosphonate complexes, which would be environmentally-persistent. Similarly, GD hydrolysis on TiO₂ yields titanium phosphonate species as detected by ³¹P MAS NMR. Attempts at obtaining ^{47,49}Ti NMR spectra of these species and those of titanium phosphonate model compounds were marginally successful. ^{47,49}Ti NMR spectra were obtainable for anatase, rutile and titanium metal; thus severe quadrupolar linebroadening is suspected for the titanium phosphonate complexes. GD reacted with aluminum and titanium powder in the presence of water results in acid-dissolution of the metals and the formation of their respective metal phosphonates.

INTRODUCTION

Inorganic oxides are currently being considered as reactive sorbents for the decontamination of chemical warfare agents (CWA).¹ Indeed, an aluminum oxide-based sorbent has recently been fielded for use on vehicles.² Another, potential application is in aircraft filtration systems to provide protection to occupants in contaminated environments.³ Besides metal oxides, the interaction of CWA with metals is also a concern in the demilitarization⁴ of bulk CWA and CWA munitions, as many chemical neutralization and/or natural degradation products are acidic and extremely corrosive to processing equipment. Finally, the identification of stable, metal-derived CWA byproducts is of potential importance to the Chemical Weapons Convention Treaty,⁵ where such materials may be uncovered during challenge inspections.

Previous work with nanosize aluminum oxide (AP-Al₂O₃)⁶ assessed the reactions of GB, GD, HD, and VX, where it was found that the products of the nerve agents formed novel aluminophosphonate compounds. Also, appropriate aluminophosphonates possessing suitable environmental stability were identified for each agent. In the current study, conventional aluminum oxide (γ-Al₂O₃) is examined and compared to the previous AP-Al₂O₃ results. Additionally, the reaction of GD with aluminum metal to form the anticipated aluminophosphonate is demonstrated. Also described are preliminary assessments of GD reactions with titanium oxide and titanium metal.

Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE 01 JUL 2003		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE 27Al, 47,49Ti, 31P, AND 13C MAS NMR Study oF VX, GB, GD And HD Reactions With Nanosize Al2O3, Al2O3, TiO2, Aluminum And Titanium				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD 21010				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES See also ADM001523.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 7	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

RESULTS AND DISCUSSION

CONVENTIONAL vs. NANOSIZE ALUMINUM OXIDE

Figures 1-3 show MAS NMR spectra⁷ obtained for GD, VX, and HD reacted with conventional γ -Al₂O₃, showing the effect of droplet size on reaction rate. For comparison, previous data is also shown for VX and HD on AP-Al₂O₃. Corresponding reaction profiles are shown in Figure 4. For GD, an identical rate ($t_{1/2} = 1.8$ h), regardless of droplet size, is observed for γ -Al₂O₃ and AP-Al₂O₃. The expected⁶ GD-derived aluminophosphonate (Al[O₂PCH₃OPin]₃) is also clearly evident both the ³¹P and ²⁷Al MAS NMR spectra as indicated. This compound only predominates at high loadings, and is thus not evident for the low-loading reaction on AP-Al₂O₃.

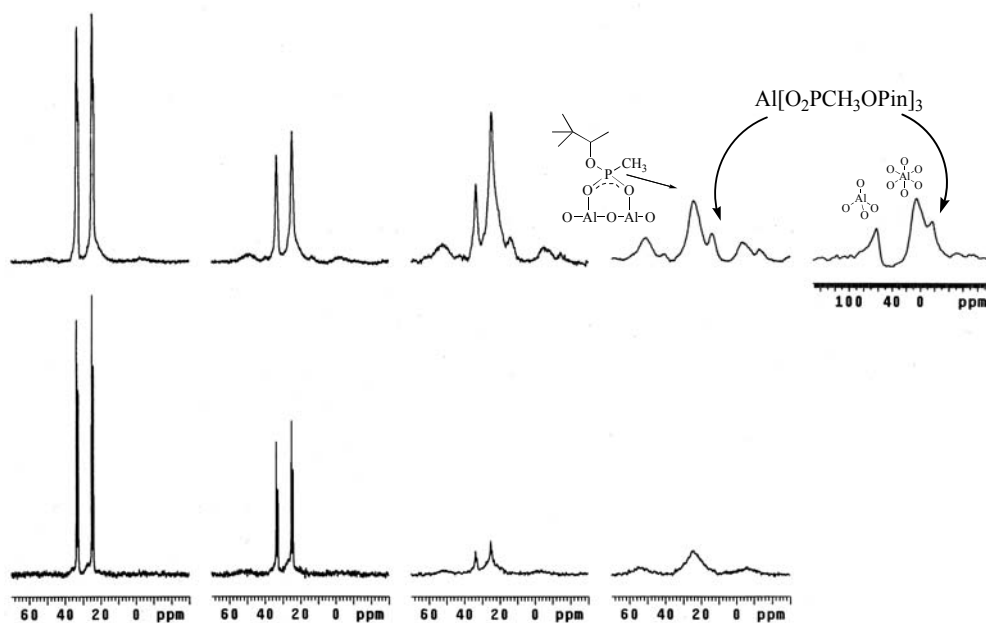


Figure 1. Selected ³¹P and ²⁷Al MAS NMR spectra obtained for 16 μ L GD on γ -Al₂O₃ (top spectra, left to right) at $t = 9$ min, 1 h, 9 h and 3 days; and 3 μ L GD on AP-Al₂O₃ (bottom spectra, left to right) at $t = 9$ min, 1 h, 4.5 h, and 1 day.

For VX, there is some dependence of the reaction rate on droplet size, with the rate of the 3.5 μ L droplets possessing nearly identical reaction rates on both γ -Al₂O₃ and AP-Al₂O₃ ($t_{1/2} = 6.8$ and 6.4 days, respectively). However, the larger droplet size on γ -Al₂O₃ yielded $t_{1/2} = 9.2$ days. The VX-derived aluminophosphonate (Al[O₂PCH₃OEt]₃) is evident for both of the reactions on γ -Al₂O₃, but not AP-Al₂O₃.

For HD, the dependence of reaction rate on droplet size is quite extreme, with the larger droplet size exhibiting $t_{1/2} = 70.9$ h, compared to $t_{1/2} = 44$ min for the smaller droplet. For the small droplet size, the rate on γ -Al₂O₃ is considerably faster than that on AP-Al₂O₃ ($t_{1/2} = 6.3$ h). However, the surface hydration state, which was not controlled, may be contributing substantially to this difference and such dramatic effects have been previously observed.⁹ Additional studies looking at hydration effects must be conducted to definitively compare the relative reactivities of the two aluminas.

The drop size-dependent reactivity behavior exhibited by the agents may be attributed to two effects: 1) smaller drops react faster owing to their large surface to volume ratio, and 2) the order of water solubility of the agents, under basic conditions, is GD > VX >> HD. Thus with its solubility in water, GD is able to

spread and react quickly across the hydrated alumina surface, and droplet size has little effect. VX has more limited water solubility, spreads more slowly, and droplet size does affect its reactivity. HD, being practically water insoluble, does not spread (at least not on a hydrated surface) and droplet size has the great affect on its reactivity. Because HD is water insoluble, surface hydration may have a profound impact its reactivity, and future studies need to be done to sort this out. Such uncontrolled hydration effects could be the cause of the apparent reactivity differences exhibited by γ - Al_2O_3 and AP- Al_2O_3 in the small droplet size experiments given above.

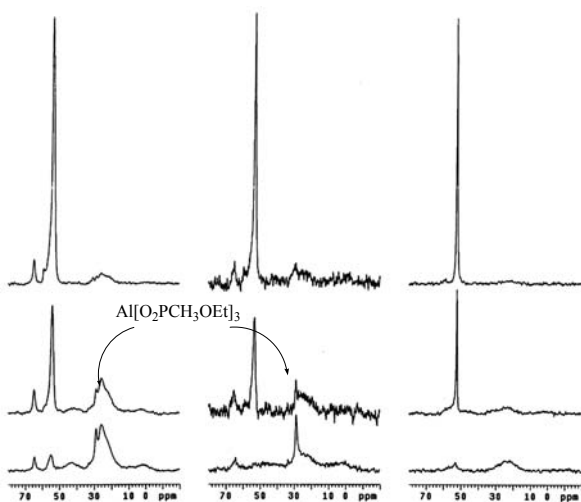


Figure 2. Selected ^{31}P MAS NMR spectra obtained for 15 μL VX on γ - Al_2O_3 (left column) at $t = 12$ min, 24 h, and 14 days; 3.5 μL VX on γ - Al_2O_3 (middle column) at $t = 14$ min, 23 h, and 17 days; and 3.5 μL VX on AP- Al_2O_3 (right column) at 12 min, 24 h, and 15 days.

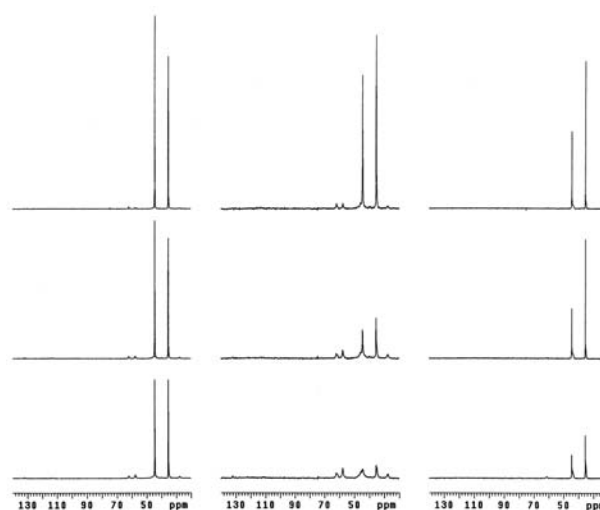


Figure 3. Selected ^{13}C MAS NMR spectra obtained for 13 μL HD on γ - Al_2O_3 (left column) at $t = 12$ min, 24 min, 1.8 h; 3.5 μL HD on γ - Al_2O_3 (middle column) at $t = 9$ min, 31 min, 2.1 h; and 3.5 μL HD on AP- Al_2O_3 (right column) at $t = 12$ min, 30 min, and 1.8 h.

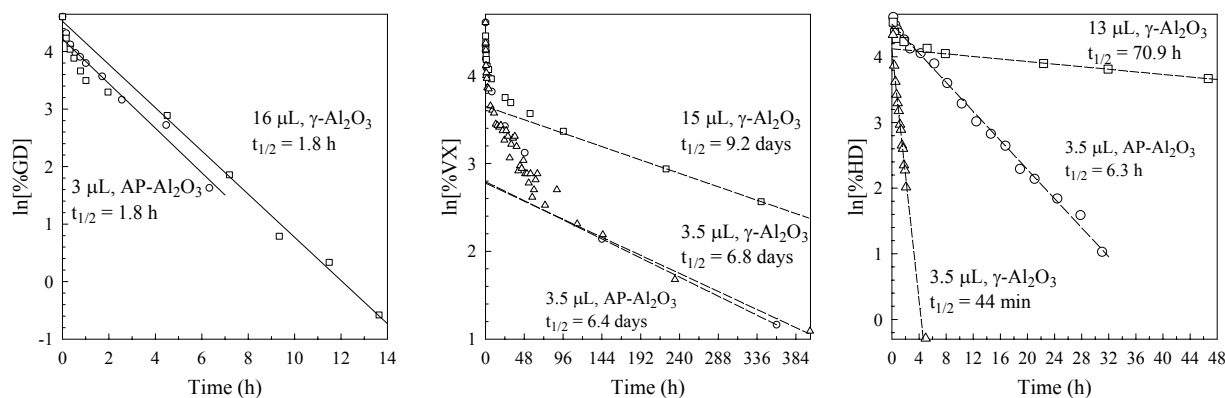


Figure 4. Reaction profiles for GD, VX, and HD reactions with γ - Al_2O_3 and AP- Al_2O_3 .

GD REACTION WITH Al METAL

Nerve agent degradation generates acidic products which have been shown to dissolve alumina to generate aluminophosphonates.⁶ Such acids would also be expected to oxidize aluminum metal ($\text{Al}_{(\text{m})}$) to generate the same products. The reaction of GD with aluminum metal powder in the presence of water does result in the quantitative formation of $\text{Al}[\text{O}_2\text{PCH}_3\text{OPin}]_3$, a white, microcrystalline powder (Figure 5). Note that a single ^{31}P MAS NMR peak is present for the compound indicative of a simple crystal structure containing only a single P-site. The ^{13}C MAS NMR spectrum shows that the pinacolyl group is still attached to the phosphonate (secondary hydrolysis of this group did not occur). The ^{27}Al MAS NMR spectrum shows residual $\text{Al}_{(\text{m})}$ at the expected Knight shift of 1640 ppm,¹⁰ and the single, sharp peak for the aluminophosphonate shows that the crystal structure possess a single, highly-symmetric Al center.

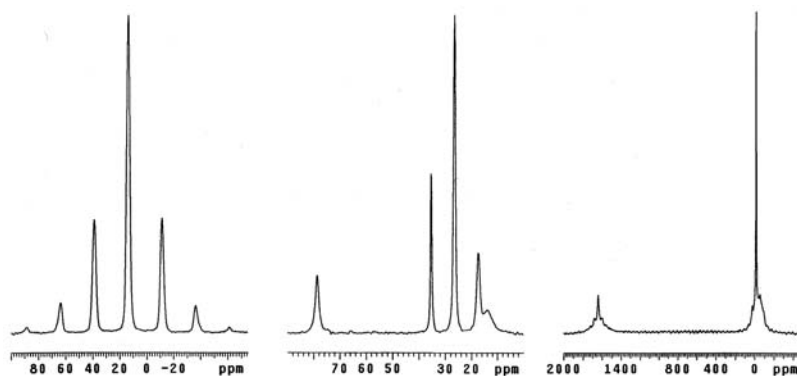


Figure 5. ^{31}P , (left to right), ^{13}C , and ^{27}Al MAS NMR spectra of GD reacted with $\text{Al}_{(\text{m})}$ in the presence of water.

TITANIUM OXIDE REACTIONS

Titanium oxide exists two common forms, rutile and anatase.¹¹ Initial work focused on their relative reactivities for GD and the formation of titanophosphonates.¹² Figure 6 shows ^{31}P NMR obtained for 50 wt% GD on anatase (loaded with 11% water) and rutile (initially without added water). In absence of added water, GD reacts only slowly on rutile; however, the addition of copious water results in the quantitative reaction to the expected hydrolysis product pinacolyl methylphosphonic acid (PMPA). GD on anatase containing 11% added water reacted swiftly, again providing quantitative conversion to PMPA. However, closer inspection of the product by ^{31}P MAS NMR resolves additional small peaks due to titanophosphonate species, some of which are soluble as shown in the CH_3CN extract of the product. The large peak in the extract is free PMPA; the small peaks are due to PMPA complexed in one or more titanophosphonate species. Unlike the corresponding aluminophosphonate, the titanophosphonate(s) possesses a more complex structure as evidenced by the multiple P-sites.

As shown in Figure 7, attempts at synthesizing the authentic titanophosphonate(s) starting with $\text{Ti}(\text{OPr})_4$ and PMPA showed that a mole ratio of one Ti^{4+} to four PMPA gave a soluble complex possessing multiple P-sites (some free PMPA is also detected). However, a mole ratio of one Ti^{4+} to two PMPA gave an immediate white precipitate with no free PMPA. ^{31}P MAS NMR shows the presence of multiple P-sites for this compound. ^{13}C MAS NMR shows that the PMPA remains intact in the complex (no hydrolysis of the pinacolyl group occurred). An attempt at obtaining a $^{47,49}\text{Ti}$ NMR¹³ spectrum of the compound yielded only a single, broad feature at -512 ppm. Such a broad peak shows that the Ti-site(s) possesses distorted symmetry.

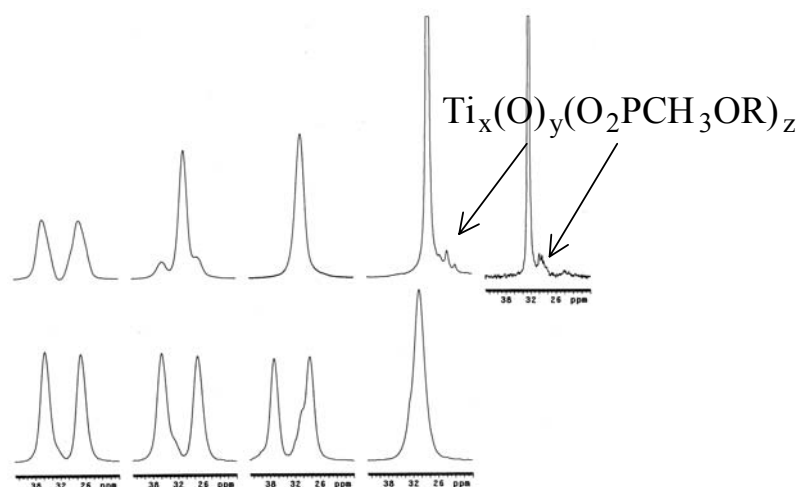


Figure 6. Selected ^{31}P and ^{31}P MAS NMR spectra of GD reactions with anatase (11% water added) (top spectra) at $t = 25$ min, 1 day, 27 days; MAS, and CH_3CN extract; and rutile (bottom spectra) at $t = 1$ day, 2 days, 7 days, and 5 days after 100% water added.

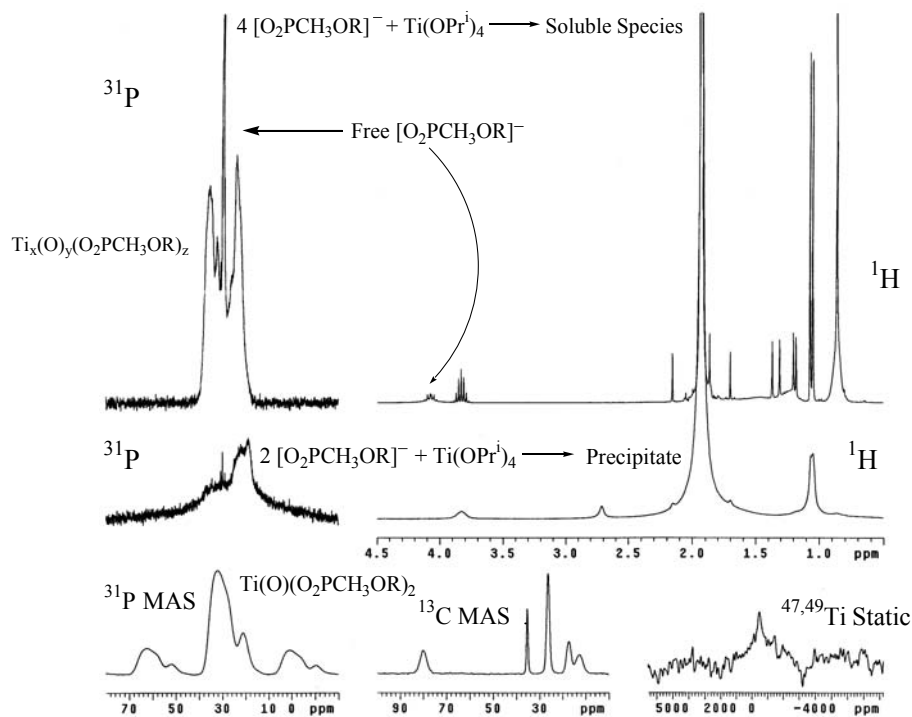


Figure 7. ^{31}P , ^1H , $^{47,49}\text{Ti}$, and ^{31}P and ^{13}C MAS NMR spectra of titanophosphonate syntheses.

GD REACTION WITH Ti METAL

Figure 8 shows NMR spectra obtained for the reaction with titanium metal powder ($\text{Ti}_{(m)}$). $\text{Ti}_{(m)}$ (0.1 g, 2.1 mmol) was mixed anatase (0.3 g, 3.8 mmol) and reacted with 193 wt% GD (0.77 mL, 4.2 mmol). ^{31}P NMR of the precipitate in contact with the reaction solution showed the formation of the titanophosphonate with very little free PMPA (sharp peak). $^{47,49}\text{Ti}$ NMR spectra taken before and after the addition of GD show the loss of the $\text{Ti}_{(m)}$ peak at the expected Knight shift¹¹ of ca. 2813 ppm and the formation of the titanophosphonate feature at -547 ppm. The anatase peak at -862 ppm also exhibited some decrease, showing that GD reacted with this material as well.

NATURE OF THE GD-TITANOPHOSPHONATE STRUCTURE

Titanophosphonates are well known in the literature,¹² many of which are soluble.¹⁴ All exhibit quite complex structures, possessing multiple Ti- and P-sites. Furthermore, frequently the Ti-sites are not symmetric. Thus it is not surprising that the structure of the GD-derived titanophosphonate is also complex, possessing multiple P-sites and that the Ti-sites have distorted symmetries. During synthesis from titanium alkoxides, titanophosphonates tend to form Ti-O-Ti bonds in addition to Ti-O-P bonds. This is due to reaction with adventitious water. Indeed, greater yields are seen with the addition of water.¹² Thus the structure of the 1:2 Ti:PMPA titanophosphonate is postulated to have the following empirical formula: $\text{Ti}(\text{O})(\text{O}_2\text{P}(\text{CH}_3)\text{OPin})_2$. Elemental analysis of the compound supports this formula. Calculated for $\text{C}_{12}\text{H}_{26}\text{O}_7\text{P}_2\text{Ti}$: C, 36.8; H, 6.7; P, 15.8; Ti, 12.2. Found: C, 35.90; H, 7.19; P, 11.67; Ti, 13.39. Work is underway to synthesize suitable crystals to enable the x-ray structure determination of the titanophosphonate.

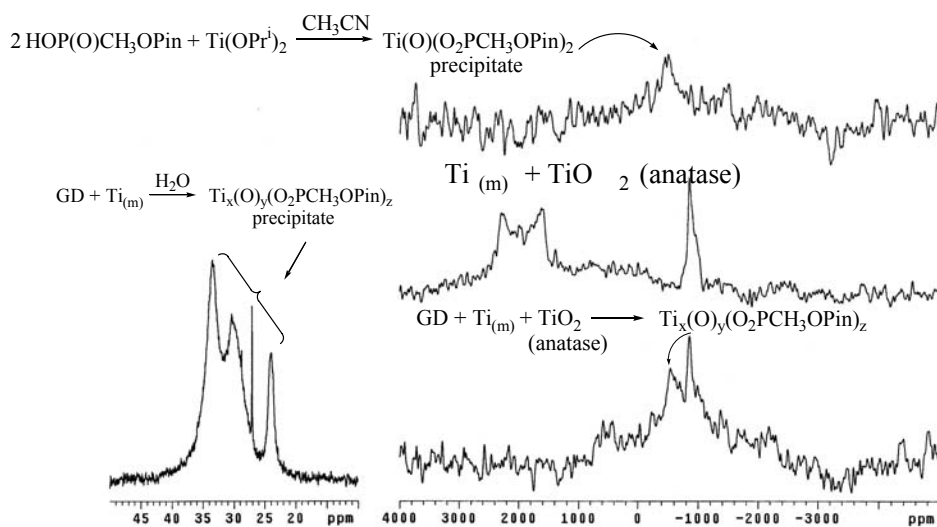


Figure 8. NMR spectra of (top, right) " $\text{Ti}(\text{O})(\text{O}_2\text{P}(\text{CH}_3)\text{OPin})_2$ " ($^{47,49}\text{Ti}$); (middle, right) $\text{Ti}_{(m)}$ + anatase ($^{47,49}\text{Ti}$); (bottom, right) GD reacted with $\text{Ti}_{(m)}$ + anatase ($^{47,49}\text{Ti}$); and (left) GD reacted with $\text{Ti}_{(m)}$ ($^{47,49}\text{Ti}$).

CONCLUSIONS

Drop size has a large effect on the reaction of VX and HD with alumina, but less effect on GD. This is attributed to the greater water solubility of GD, which allows it to spread more readily on the hydrated alumina surface. GD reacts with $\text{Al}_{(m)}$ to form the same aluminophosphonate, $\text{Al}[\text{O}_2\text{PCH}_3\text{OPin}]_3$, derived from aluminum oxide. GD reacts with rutile, anatase, and $\text{Ti}_{(m)}$ to yield titanophosphonate(s). The formula of the GD-derived titanophosphonate is postulated to be $\text{Ti}(\text{O})(\text{O}_2\text{P}(\text{CH}_3)\text{OPin})_2$, in agreement with elemental analysis data.

ACKNOWLEDGEMENT

We thank Mr. John Mahle for many helpful discussions.

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